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MECHANISM OF INSERTION IN HIGHLY CONDUCTING GRAPHITE INTERCALAT--ETC(U)

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## BRIEF OUTLINE OF RESEARCH FINDINGS

### RESEARCH GOALS

The research was initiated with a three-fold purpose: (1) determine the mechanism of preparation of graphite intercalation (in particular the so-called acceptor compounds); (2) to relate structure and properties of these compounds; and (3) to prepare new intercalation compounds of high electrical conductivity. The proposal indicated that the focus of the research could be on intercalation by  $\text{HNO}_3$ ,  $\text{SbF}_5$  and  $\text{FeCl}_3$ .

### SUMMARY OF RESULTS

Research supported by this grant was instrumental in leading to the conclusion that virtually all graphite intercalation reactions that give acceptor compounds are oxidation reactions. In the case of  $\text{HNO}_3$  intercalation, graphite is oxidized by  $\text{NO}_2^+$  ions with formation of free  $\text{NO}_2$  and insertion of  $\text{HNO}_3$  and  $\text{NO}_3^-$ . In the case of intercalation by antimony pentafluoride, the  $\text{SbF}_5$  oxidizes the lattice and is reduced to  $\text{SbF}_3$  (which is excluded from the lattice);  $\text{SbF}_6^-$  ions and  $\text{SbF}_5$  molecules are inserted during the process.

In the case of the nitric acid intercalation compound, it was established that the neutral  $\text{HNO}_3$  molecules are labile and can be moved in and out of the lattice by varying the partial pressure of  $\text{HNO}_3$  in equilibrium with the intercalation compound. An extraordinarily important observation was that, to a first approximation, the electrical conductivity of the intercalation compound is independent of neutral molecule content.

Work on the mechanism of intercalation by  $\text{FeCl}_3$  was, on the one hand frustrating and inconclusive, but on the other hand led to a significant discovery. One can postulate that  $\text{FeCl}_3$  could oxidize graphite, be reduced to  $\text{FeCl}_2$  and insert  $\text{FeCl}_4^-$  along with  $\text{FeCl}_3$  neutral molecules. Also,  $\text{FeCl}_3$  gives  $\text{FeCl}_2$  and  $\text{Cl}_2$  upon heating. The  $\text{FeCl}_3$  and  $\text{Cl}_2$  could form a complex  $\text{FeCl}_4^- \dots \text{Cl}^+$  which could oxidize the graphite lattice through the chlorine cation - against inserting  $\text{FeCl}_4^-$  ions. Finally,  $\text{FeCl}_2$  solid and  $\text{FeCl}_3$  vapor are in equilibrium with  $\text{Fe}_2\text{Cl}_8$  gas, which, if it were inserted, would effectively intercalate  $\text{FeCl}_2$ . Much effort in developing analytical techniques for establishing the stoichiometry failed to pin down this mechanism. Our best interpretation of the data is that both mechanisms are operative, leading to confusing results.

To cast more light on the nature of  $\text{FeCl}_3$  intercalation compounds, we invented a new method of inserting  $\text{FeCl}_4^-$  ions. Adducts can be prepared from  $\text{FeCl}_3$  and  $\text{NOCl}$ . They are low melting partially covalent salts with a formula  $\text{NOFeCl}_4$ . They react with graphite giving highly conductive compounds. In this case,  $\text{FeCl}_4^-$  is the only plausible ion that could have been inserted.

Finally, we conclude from many of our experiments that attack of the oxidizing agent is on the pi electron system in the basal planes.



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## PUBLICATIONS

1. "Conditions for Intercalation of Graphite with Pure Nitric Acid", W.C. Forsman, J. Hoffman and F.L. Vogel, paper presented at annual meeting of American Chemical Society, New Orleans, March 27-30, 1977.
2. "Electrical Resistivity of Graphite Nitrates", F.L. Vogel, C. Zeller and W.C. Forsman, Ext. Abs. Prog., 13th Bienn. Conf. Carbon, 151 (1977).
3. "Chemistry of Graphite Intercalation by Nitric Acid", W.C. Forsman, F.L. Vogel, D.E. Carl and J. Hoffman, Carbon 16, 269 (1978).
4. "Electrical Resistivity of Graphite Intercalated with Ferric Chloride", (abstract), J.B. Perrachon, C. Zeller and F.L. Vogel, Bull. A.P.S. 23, 219
5. "Electrical Conductivity of Graphite Intercalated with Ferric Chloride", J.B. Perrachon, C. Zeller and F.L. Vogel, Ext. Abs. Prog., 14th Bienn. Conf. Carbon, 304 (1979).
6. "Mobility of Spacer Molecules in Graphite Nitrate", W.C. Forsman, D.E. Carl and F.L. Vogel, Mat. Sci. Eng. 8, 53 (1980).
7. "Oxidative Intercalation of Graphite by Antimony Pentafluoride", W.C. Forsman, D.E. Carl and T. Birchall, Ext. Abs. Prog., 15th Bienn. Conf. Carbon, 353 (1981).
8. "Vapor Phase Intercalation by  $AlCl_3$ -HCl Mixtures", K. Leong and W.C. Forsman, Ext. Abs. Prog., 15th Bienn. Conf. Carbon, 356 (1981).
9. "Intercalation of Graphite with the Adducts of Nitronyl Chloride and Metal Chlorides", K. Leong, W.C. Forsman and F.L. Vogel, Ext. Abs. Prog., 15th Bienn. Conf. Carbon, 398 (1981).

### LIST OF PERSONNEL SUPPORTED

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### LIST OF DEGREES AWARDED

Master of Science of Engineering (M.S.E.) Degree in Chemical Engineering  
awarded to Jeffery Hoffman, 1976.

M.S.E. in Chemical Engineering awarded to Theodore Dziemianowicz, August, 1980.